Dalton Transactions

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2013, **42**, 15625

Multi-pyridine decorated Fe(II) and Ru(II) complexes by Pd(0)-catalysed cross couplings: new building blocks for metallosupramolecular assemblies†

Jiajia Yang,[a] Jack K. Clegg,[b] Qibai Jiang,[a] Xiaoming Lui,[c] Hong Yan,[a] Wei Zhong[c] and Jonathon E. Beves*[a,d]

Received 26th August 2013,
Accepted 1st September 2013

DOI: 10.1039/c3dt52331d

www.rsc.org/dalton

Eight metal complexes of the type $[M(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2′′-terpyridine) featuring four pendant pyridine rings are reported and characterised by NMR, MS, absorption spectroscopy and electrochemical methods. Palladium-mediated Suzuki and Sonogashira cross-coupling reactions were performed on both free 4′-(3,5-dibromophenyl)-tpy and its Ru(II) complex in good yields. The ready *N*-alkylation of the pendant pyridyl units has significant influence on the absorption and electrochemical reduction of the complexes, processes which are localised on the periphery and leaves the $[Ru(tpy)_2]^{2+}$ core essentially unaffected. The binding of metal ions by the free pyridines is also demonstrated as means of assembling larger ordered non-covalent structures.

Introduction

The development of ligands with groups capable of selective and predictable binding of multiple metal ions has offered a wealth of opportunities for the self-assembly of coordination cages,[1] helicates,[2] metallopolymers,[3] networks[4] and other supramolecular architectures[5] with increasingly impressive applications.[6] Incorporating the rich chemistry of metal complexes into larger structures remains a key goal for materials and supramolecular chemists. The 'expanded ligand'[7] approach employs complexes decorated with pendant binding sites to achieve this objective.[8]

One the most studied classes of complexes are the Ru(II) polypyridyl complexes due to their electronic,[9] catalytic, photophysical properties,[10] bio-applications,[11] applications in functional polymers,[4b,12] coordination networks,[13] and molecular machines.[14] For many of these applications the orientation or separation of appended functionalities in well-defined relative conformations is a requirement for controlling their interactions and the resulting molecular or material properties. Towards this goal, we sought to introduce pendant binding groups onto 4′(-phenyl)tpy (tpy = 2,2′:6′:2″-terpyridine) ligands *via* rigid linkers which nonetheless remain electronically isolated from the metal centre and may allow use as building blocks for larger assemblies. A suitable means of constructing these structures is *via* palladium(0)-catalysed Suzuki[15] or

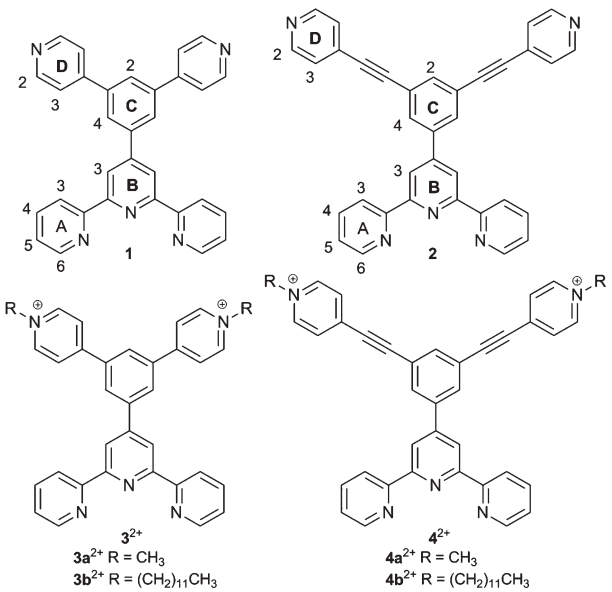


Fig. 1 Structure of ligands in this study, showing the numbering scheme adopted.

[a]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*
[b]*School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane St Lucia, QLD 4072, Australia*
[c]*College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing 314001, China*
[d]*School of Chemistry, The University of New South Wales (UNSW), Sydney NSW 2052, Australia. E-mail: j.beves@unsw.edu.au*

†Electronic supplementary information (ESI) available: Detailed experimental procedures and characterisation, NMR, ESI-MS, UV-vis spectra and CV data. CCDC 948457, 948463–948465. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52331d

Sonogashira couplings.[16] Suzuki coupling between mono-haloterpyridine derivatives[17] and boronic acids or esters, as well as upon their metal complexes is well established,[18] and Sonogashira couplings on polypyridine derivatives have been also reported.[19,20] Herein we report eight new Fe(II) or Ru(II) complexes of 2,2′:6′:2″-terpyridine metal complexes of the type $[M(tpy)_2]^{2+}$ which feature multiple pendant pyridyl groups (ligands **1–4**, Fig. 1), prepared using Suzuki and Sonogashira couplings. The reactivity of these pendant pyridyl groups towards alkylating agents is investigated and a detailed electrochemical and photophysical study of the influence of these interactions on the redox and electronic properties of the complexes is presented. Finally, the ability of these pendant groups to bind additional metal centres is explored.

Experimental

General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer; the numbering scheme adopted for the ligands is shown in Fig. 1. For the NMR spectra of complexes containing ligands **1** or **2**, Et_3N was added to the solution to confirm that the coordinated ligands were fully deprotonated. Electrospray ionisation (ESI) mass spectra were recorded using a Finnigan MAT LCQ mass spectrometer. Electronic absorption spectra were recorded on an Agilent 8453 UV-Visible Spectrophotometer. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 system using glassy carbon working and platinum auxiliary electrodes with a silver wire as a pseudoreference electrode; purified MeCN was used as the solvent and 0.1 M $[n\mathrm{Bu_4N}][PF_6]$ as the supporting electrolyte; ferrocene was added at the end of each experiment as an internal reference. Compounds 4′-(3,5-dibromophenyl)-2,2′:6′,2″-terpyridine (**5**),[21] 4-ethynylpyridine,[22] 4-pyridineboronic acid pinacol ester[23] and $Ru(DMSO)_4Cl_2$[24] were prepared by literature methods. Additional details are found in the ESI.†

Ligand 1

4′-(3,5-Dibromophenyl)-2,2′:6′,2″-terpyridine (200 mg, 0.43 mmol), 4-pyridineboronic acid pinacol ester (0.26 g, 1.3 mmol, 3 equiv.) and $CsCO_3$ (0.83 g, 4.3 mol 10 equiv.) were dissolved in degassed DMF (10 mL). The solution was bubbled with argon for 10 min. $Pd(PPh_3)_4$ (100 mg, 0.09 mmol, 20%) was added quickly and the solution was bubbled with argon for another 10 min. The solution was stirred at 80 °C for 12 h. The solvent was removed to give a pale yellow sludge which was dissolved in 10% MeOH in DCM (30 mL) and absorbed on SiO_2. Column chromatography (SiO_2, DCM–MeOH–NEt_3 100 : 2 : 0.001) gave the title compound as a white solid (170 mg, 0.55 mmol, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (s, 2H, H^{B3}), 8.79–8.73 (m, 6H, H^{A6+D2}), 8.72 (d, J = 8.0 Hz, 2H, H^{A3}), 8.17 (s, 2H, H^{C4}), 7.95–7.88 (m, 3H, H^{A4+C2}), 7.67 (d, J = 4.5 Hz, 4H, H^{D3}), 7.42–7.36 (m, 2H, H^{A5}). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.4 (C^{B2}), 156.1 (C^{A2}), 150.6 (C^{D2}), 149.5 (C^{C5}), 149.3 (C^{A6}), 147.7 (C^{C1}), 141.0 (C^{B4}), 140.3 (C^{D4}), 137.2 (C^{A4}), 126.8 (C^{C4}), 126.4 (C^{C2}), 124.3 (C^{A5}), 122.1 (C^{D3}), 121.6 (C^{A3}), 119.1 (C^{B3}). LR-ESI-MS m/z found 464.42 (LH^+), requires 464.19 m/z. HR-ESI-MS found 464.1873 (LH^+) requires: 464.1870. M.p. 260–262 °C.

Ligand 2

4′-(3,5-Dibromophenyl)-2,2′:6′,2″-terpyridine (100 mg, 0.21 mmol) and 4-ethynylpyridine (62 mg, 0.6 mmol, 3 equiv.) was dissolved in degassed (three freeze–pump–thaw cycles) THF (15 mL) and freshly distilled diethylamine (5 mL), the solution was bubbled with argon for 10 min. $Pd(PPh_3)_4$ (50 mg, 0.04 mmol, 20%) were added quickly and bubbled with argon for another 10 min. The solution was stirred at reflux for 24 h. The solvent was removed to give a yellow sludge which was dissolved in ethyl acetate (30 mL) and absorbed on SiO_2. Column chromatography (SiO_2, petroleum ether–ethyl acetate–NEt_3 5 : 2 : 0.001) gave the title compound as a white solid (90 mg, 0.18 mmol, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (m, 4H, H^{A6+B3}), 8.71 (d, J = 7.9 Hz, 2H, H^{A3}), 8.65 (dd, J = 4.5, 1.5 Hz, 4H, H^{D2}), 8.11 (d, J = 1.4 Hz, 2H, H^{C4}), 7.91 (td, J = 7.8, 1.7 Hz, 2H, H^{A4}), 7.83 (t, J = 1.3 Hz, 1H, H^{C2}), 7.44 (dd, J = 4.5, 1.5 Hz, 4H, H^{D3}), 7.39 (ddd, J = 7.4, 4.6, 1.0 Hz, 2H, H^{A5}). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.4 (C^{B2}), 156.0 (C^{A2}), 150.1 (C^{D2}), 149.3 (C^{A6}), 148.4 (C^{C5}), 139.8 (C^{B4}), 137.2 (C^{A4}), 135.3 (C^{C2}), 131.3 (C^{C4}), 131.0 (C^{D4}), 125.7 (C^{D3}), 124.3 (C^{A5}), 123.7 (C^{C1}), 121.6 (C^{A3}), 118.8 (C^{B3}), 92.4 ($C^{C\text{-alkyne}}$), 88.1 ($C^{D\text{-alkyne}}$). LR-ESI-MS m/z found 511.5 (LH^+) requires 512.2 m/z. HR-ESI-MS found 512.1882, requires 512.1870. M.p. 304–306 °C.

$[Fe(\mathbf{1})_2](PF_6)_2$

Ligand **1** (22 mg, 0.043 mmol) and $FeCl_2{\cdot}4H_2O$ (4 mg, 0.02 mmol) were dissolved in EtOH (20 mL) and the reaction mixture was stirred at room temperature for 1 h. Excess ethanolic NH_4PF_6 was added and the resulting purple precipitate was collected on Celite and washed well with water (3 × 10 mL), EtOH (2 × 2 mL) and Et_2O (20 mL). The residue was dissolved in MeCN and the solvent removed to give $[Fe(\mathbf{1})_2][PF_6]_2$ as a purple powder (25 mg, 0.019 mmol, 90%). ^{1}H NMR (500 MHz, CD_3CN) δ 9.38 (s, 2H, H^{B3}), 8.82 (d, J = 5.6 Hz, 4H, H^{D2}), 8.72 (m, 4H, H^{C4+A3}), 8.39 (s, 1H, H^{C2}), 8.01 (d, J = 5.7 Hz, 4H, H^{D3}), 7.95 (t, J = 7.6 Hz, H^{A4}), 7.23 (d, J = 5.5 Hz, 2H, H^{A6}), 7.13 (t, J = 6.5 Hz, H^{A5}). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN) δ 161.4 (C^{B2}), 158.9 (C^{A2}), 154.0 (C^{A6}), 151.5 (C^{D2}), 150.3 (C^{C5}), 147.8 (C^{C1}), 141.4 (C^{D4}), 139.8 (C^{A4}), 139.6 (C^{B4}), 128.8 (C^{C2}), 128.4 (C^{A5}), 128.1 (C^{C4}), 125.0 (C^{A3}), 123.0 (C^{B3+D3}). LR-ESI-MS m/z 491.58 $[M - 2PF_6]^{2+}$ requires 491.15, 1127.67 $[M - PF_6]^+$ requires 1127.26; HR-MS m/z 491.1492 $[M - 2PF6]^{2+}$ requires 491.1495.

$[Fe(\mathbf{2})_2](PF_6)_2$

The preparation for $[Fe(\mathbf{2})_2](PF_6)_2$ was the same as for $[Fe(\mathbf{1})_2](PF_6)_2$, starting with ligand **2** (20 mg, 0.043 mmol) and

$FeCl_2{\cdot}4H_2O$ (4 mg, 0.02 mmol) to give $[Fe(\mathbf{2})_2][PF_6]_2$ as a purple powder (24 mg, 0.019 mmol, 90%). ^{1}H NMR (500 MHz, CD_3CN) δ 9.26 (s, 2H, H^{B3}), 8.69 (d, J = 4.5 Hz, 4H, H^{D2}), 8.66 (d, J = 8.0 Hz, 2H, H^{A3}), 8.59 (s, 2H, H^{C4}), 8.12 (s, 1H, H^{C2}), 7.95 (t, J = 7.7 Hz, 2H, H^{A4}), 7.58 (d, J = 4.5 Hz, 4H, H^{D3}), 7.21 (d, J = 5.5 Hz, 2H, H^{A6}), 7.12 (t, J = 6.5 Hz, 2H, H^{A5}). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN) δ 161.5 (C^{B2}), 158.8 (C^{A2}), 154.0 (C^{A6}), 151.1 (C^{D2}), 149.1 (C^{C5}), 139.8 (C^{A4}), 139.0 (C^{B4}), 137.0 (C^{C2}), 132.7 (C^{C4}), 131.2 (C^{D4}), 128.4 (C^{A5}), 126.4 (C^{D3}), 125.1 (C^{C1}), 124.9 (C^{A3}), 122.6 (C^{B3}), 92.3 ($C^{C\text{-alkyne}}$), 89.2 ($C^{D\text{-alkyne}}$). LR-ESI-MS m/z found 539.67 $[M - 2PF_6]^{2+}$, requires 539.15 m/z, $[M - PF_6]^+$ 1223.68 requires 1223.26; HR-ESI-MS found 539.1488 $[M - 2PF_6]^{2+}$ requires 539.1495.

$[Ru(\mathbf{5})_2](PF_6)_2$

4′-(3,5-Dibromophenyl)-2,2′:6′,2″-terpyridine (**5**) (0.40 g, 085 mmol) and $Ru(DMSO)_4Cl_2$ (0.19 g, 0.39 mmol) were suspended in ethane-1,2-diol (30 mL) and heated in a microwave (800 W, 140 degrees, 10 min). The deep red solution was cooled to room temperature and poured into excess aqueous NH_4PF_6 (100 mL). The resulting red precipitate was collected on Celite and washed well with water (3 × 100 mL), EtOH (2 × 10 mL), $CHCl_3$ (3 × 50 mL) and Et_2O (20 mL). The remaining residue was dissolved in MeCN and the solvent removed to give $[Ru(\mathbf{5})_2][PF_6]_2$ as a deep red powder (0.51 g, 0.38 mmol, 97%). This was purified by column chromatography (SiO_2, MeCN–H_2O–saturated aqueous KNO_3 14 : 1 : 1). The centre of the main red band was collected, excess aqueous NH_4PF_6 was added and the volume reduced to precipitate the hexafluorophosphate salt, which was collected and recrystallised from MeCN–H_2O to give a pure microcrystalline red solid (0.46 g, 0.35 mmol, 90%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.00 (s, 2H, H^{B3}), 8.66 (d, J = 8.1 Hz, 2H, H^{A3}), 8.41 (d, J = 1.7 Hz, 2H, H^{C4}), 8.06 (s, 1H, H^{C2}), 7.96 (td, J = 7.9, 1.4 Hz, 2H, H^{A4}), 7.41 (d, J = 5.6 Hz, 2H, H^{A6}), 7.19 (ddd, J = 7.2, 5.6, 1.0 Hz, 2H, H^{A5}). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ 158.8 (C^{A2}), 156.5 (C^{B2}), 153.4 (C^{A6}), 146.0 (C^{C5}), 141.4 (C^{B4}), 139.1 (C^{A4}), 136.1 (C^{C2}), 130.7 (C^{C4}), 128.5 (C^{A5}), 125.6 (C^{A3}), 124.7 (C^{C1}), 122.7 (C^{B3}). LR-ESI-MS m/z 518.17 $[M - 2PF_6]^{2+}$ requires 517.90; 1180.67 $[M - PF_6]^+$ requires 1180.77; HR-MS m/z 517.9042 $[M(\mathbf{L})_2]^{2+}$ requires 517.9014, 1180.7652 $[M(L)_2(PF_6)]^+$ requires 1180.7670.

$[Ru(\mathbf{1})_2](PF_6)_2$

$[Ru(\mathbf{5})_2](PF_6)_2$ (0.32 g, 0.24 mmol), 4-pyridineboronic acid pinacol ester (0.30 g, 1.45 mmol, 6 equiv.), $CsCO_3$ (0.93 g, 4.8 mmol) and NH_4PF_6 (0.32 g, 1.9 mol) was dissolved in degassed DMF (20 mL). The solution was bubbled with argon for 10 min. $Pd(PPh_3)_4$ (60 mg, 0.05 mmol, 20%) was added quickly and bubbled with argon for another 10 min. The solution was stirred at 80 °C overnight. The solvent was removed and the residue dissolved in 5 mL MeCN, poured into excess aqueous NH_4PF_6 (100 mL). The resulting red precipitate was collected on Celite and washed well with water (3 × 100 mL), EtOH (2 × 10 mL) and Et_2O (20 mL). The remaining residue was dissolved in MeCN. The solvent was removed to give a red powder which was absorbed on SiO_2 and purified by column chromatography (SiO_2, MeCN–H_2O–saturated aqueous KNO_3 7 : 1 : 1) gave the title compound $[Ru(\mathbf{1})_2](PF_6)_2$ as a red solid (268 mg, 0.19 mmol, 85%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.20 (s, 2H, H^{B3}), 8.81 (d, J = 4.6, 1.6 Hz, 4H, H^{D2}), 8.74 (d, J = 8.2 Hz, 2H, H^{A3}), 8.61 (d, J = 1.5 Hz, H^{C4}), 8.35 (t, J = 1.5 Hz, H^{C2}), 8.03–7.94 (m, 6H, H^{D3+A4}), 7.47 (d, J = 4.9 Hz, 2H, H^{A6}), 7.22 (t, J = 6.6 Hz, 2H, H^{A5}). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ 159.1 (C^{A2}), 156.5 (C^{B2}), 153.4 (C^{A6}), 151.4 (C^{D2}), 148.2 (C^{C5}), 147.8 (C^{C1}), 141.3 (C^{D4}), 139.7 (C^{B4}), 139.1 (C^{A4}), 128.5 (C^{C2+A5}), 128.0 (C^{C4}), 125.6 (C^{A3}), 123.0 (C^{B3+D3}). LR-ESI-MS m/z 514.40 $[M - 2PF_6]^{2+}$ requires 514.13, 1173.44 $[M - PF_6]^+$ requires 1173.23; HR-MS m/z 514.1331 $[M - 2PF_6]^{2+}$ requires 514.1335; 1173.2303 $[M - PF_6]^+$ requires 1173.2311.

$[Ru(\mathbf{2})_2](PF_6)_2$

$[Ru(\mathbf{5})_2](PF_6)_2$ (100 mg, 0.08 mmol), 4-ethynylpyridine (0.62 g, 0.60 mmol, 8 equiv.), CuI (0.8 mg, 0.045 mmol, 60%) and NH_4PF_6 (20 mg, 0.12 mol) was dissolved in degassed DMF (5 mL) and DME (10 mL). The solution was bubbled with argon for 10 min. $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 40%) was added quickly and bubbled with argon for another 10 min. The solution was stirred at 80 °C overnight. The solution was bubbled with argon for 10 min. $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 40%) was added quickly and bubbled with argon for another 10 min. The solution was stirred at 70 °C overnight. The solvent was removed and the residue dissolved in 5 mL MeCN, poured into excess aqueous NH_4PF_6 (100 mL). The resulting red precipitate was collected on Celite and washed well with water (3 × 100 mL), EtOH (2 × 10 mL) and Et_2O (20 mL). The remaining residue was dissolved in MeCN. The solvent was removed to give a red powder which was absorbed on SiO_2 and purified by column chromatography (SiO_2, MeCN–H_2O–saturated aqueous KNO_3 10 : 1 : 1) gave the title compound $[Ru(\mathbf{2})_2](PF_6)_2$ as a red solid (82 mg, 0.058 mmol, 77%) ^{1}H NMR (400 MHz, CD_3CN) δ 9.09 (s, 2H, H^{B3}), 8.75–8.65 (m, 6H, H^{D2+A3}), 8.49 (d, J = 1.1 Hz, 2H, H^{C4}), 8.07 (s, 1H, H^{C2}), 7.98 (t, J = 7.4 Hz, 2H, H^{A4}), 7.56 (dd, J = 4.6, 1.4 Hz, 4H, H^{D3}), 7.45 (d, J = 5.3 Hz, 2H, H^{A6}), 7.22 (t, 2H, H^{A5}). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ 158.9 (C^{A2}), 156.6 (C^{B2}), 153.4 (C^{A6}), 151.1 (C^{D2}), 147.0 (C^{C5}), 139.2 (C^{A4}), 139.1 (C^{B4}) 136.8 (C^{C2}), 132.6 (C^{C4}), 131.2 (C^{D4}), 128.6 (C^{A5}), 126.4 (C^{D3}), 125.6 (C^{A3}), 125.0 (C^{C1}), 122.7 (C^{B3}), 92.3 ($C^{C\text{-alkyne}}$), 89.1 ($C^{D\text{-alkyne}}$). LR-ESI-MS m/z 562.34 $[M - 2PF_6]^{2+}$ requires 562.13, 1269.34 $[M - PF_6]^+$ requires 1269.23; HR-MS m/z 562.1340 $[M - 2PF_6]^{2+}$ requires 562.1335, 1269.23096 $[M - PF_6]^+$ requires 1269.2306.

$Ru(\mathbf{3a})_2](PF_6)_6$

$[Ru(\mathbf{1})_2](PF_6)_2$ (20 mg, 0.015 mmol), NH_4PF_6 (60 mg, 0.2 mmol) and methyl iodide (1 mL, 7 mmol) dissolved in 30 mL MeCN. The solution was refluxed overnight to give a red suspension. Water was added and the volume reduced under reduced pressure. The resulting suspension was collected on Celite, washed well with water, EtOH, DCM and Et_2O. The residue was dissolved in MeCN and the solvent removed to give the title compound $[Ru(\mathbf{3a})_2](PF_6)_6$ as a red solid (30 mg, 0.015 mmol, 99%). ^{1}H NMR (500 MHz, CD_3CN) δ 9.24 (s, 2H,

H^{B3}), 8.91 (s, 2H, H^{C4}), 8.86 (d, J = 6.5 Hz, 4H, H^{D2}), 8.78 (d, J = 8.1 Hz, 2H, H^{A3}), 8.66 (d, J = 6.5 Hz, 4H, H^{D3}), 8.63 (s, 1H, H^{C2}), 8.01 (t, J = 7.8 Hz, 2H, H^{A4}), 7.52 (d, J = 5.5 Hz, 2H, H^{A6}), 7.25 (t, J = 6.4 Hz, 2H, H^{A5}), 4.42 (s, 6H, H^{Me}). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) δ 158.9 (C^{A2}), 156.6 (C^{B2}), 155.3 (C^{C1}), 153.4 (C^{A6}), 146.8 (C^{C5}), 146.6 (C^{D2}), 140.8 (C^{B4}), 139.2 (C^{A4}), 137.7 (C^{D4}), 131.3 (C^{C4}), 130.1 (C^{C2}), 128.6 (C^{A5}), 126.7 (C^{D3}), 125.6 (C^{A3}), 123.1 (C^{B3}), 48.8 (Me). LR-ESI-MS found m/z 181.75 $[M - 6PF_6]^{6+}$, requires 181.39; 247.00 $[M - 5PF_6]^{5+}$ requires 246.66; 344.75 $[M - 4PF_6]^{4+}$ requires 344.57; 507.58 $[M - 3PF_6]^{3+}$ requires 507.75; 834.08 $[M - 2PF_6]^{2+}$ requires 834.11. HR-ESI-MS m/z found 181.3939 $[M - 6PF_6]^{6+}$ requires 181.3935; 246.6135 $[M - 5PF_6]^{5+}$ requires 246.6650; 344.5726 $[M - 4PF_6]^{4+}$ requires 344.5723; 507.7520 $[M - 3PF_6]^{3+}$ requires 507.7511; 834.1093 $[M - 2PF_6]^{2+}$ requires 834.1088.

$[Ru(3b)_2](PF_6)_6$

$[Ru(\mathbf{1})_2](PF_6)_2$ (20 mg, 0.015 mmol), NH_4PF_6 (60 mg, 0.2 mmol) and 1-iodododecane (3 mL, 10 mmol) were dissolved in MeCN (30 mL) and heated at reflux for 2 days. The solvent was removed under reduced pressure and the crude red powder was purified by column chromatography (SiO_2, MeCN–H_2O–saturated aqueous KNO_3 14 : 1 : 1). The centre of the main red band was collected, excess aqueous NH_4PF_6 was added and the volume reduced to precipitate the hexafluorophosphate salt which was collected on Celite and washed with water and EtOH (slightly soluble). The complex was dissolved in DCM and hexane was added to precipitate the complex, which was collected on Celite and washed well with hexane. The residue was dissolved in MeCN and the solvent removed to give the title compound $[Ru(\mathbf{3b})_2](PF_6)_6$ as a red solid (20 mg, 0.008 mmol, 53%). ^1H NMR (500 MHz, CD_3CN) δ 9.22 (s, 2H, H^{B3}), 9.01–8.84 (m, 6H, H^{C4+D2}), 8.76 (d, J = 8.1 Hz, 2H, H^{A3}), 8.66 (d, J = 6.5 Hz, 4H, H^{D3}), 8.61 (s, 1H, H^{C2}), 8.01 (t, J = 7.8 Hz, 2H, H^{A4}), 7.50 (d, J = 5.5 Hz, 2H, H^{A6}), 7.25 (t, J = 6.5 Hz, 2H, H^{A5}), 4.63 (t, J = 7.5 Hz, 4H, H^{a}), 2.15–2.00 (m, 4H, H^{b}), 1.49–1.36 (m, 4H, H^{alk}, 1.37–1.22 (m, 14H, H^{alk}), 0.88 (t, J = 6.7 Hz, 6H, H^{l}) (H^{alk} = H^{d-i}). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) δ 158.9 (C^{A2}), 156.6 (C^{B2}), 155.6 (C^{C1}), 153.4 (C^{A6}), 146.8 (C^{C5}), 145.7 (C^{D2}), 140.8 (C^{B4}), 139.2 (C^{A4}), 137.8 (C^{D4}), 131.4 (C^{C4}), 130.1 (C^{C2}), 128.6 (C^{A5}), 127.0 (C^{D3}), 125.7 (C^{A3}), 123.0 (C^{B3}), 62.4 (C^{a}), 32.5 (C^{j}), 31.8 (C^{b}), 30.2 (C^{alk} × 2), 30.1 (C^{alk}), 30.0 (C^{alk} × 2), 29.6 (C^{alk}), 26.6 (C^{c}), 23.3 (C^{k}), 14.3 (C^{l}). (C^{alk} = C^{d-i}). LR-ESI-MS found m/z 284.75 $[M - 6PF_6]^{6+}$, requires 284.17, m/z 370.33 $[M - 5PF_6]^{5+}$ requires 370.00, m/z 499.17 $[M - 4PF_6]^{4+}$ requires 498.74, m/z 713.50 $[M - 3PF_6]^{3+}$ requires 713.31, m/z 1142.58 $[M - 2PF_6]^{2+}$ requires 1142.45; HR-ESI-MS found, 370.0033 $[M - 5PF_6]^{5+}$ requires 370.0027, 498.7446 $[M - 4PF_6]^{4+}$ requires 498.7445; 713.3148 $[M - 3PF_6]^{3+}$ requires 713.3140; 1142.4516 $[M - 2PF_6]^{2+}$ requires 1142.4531.

$[Ru(4a)_2](PF_6)_6$

The preparation for $[Ru(\mathbf{4a})_2](PF_6)_6$ was the same as for $[Ru(\mathbf{3a})_2](PF_6)_6$, starting from $[Ru(\mathbf{2})_2](PF_6)_2$ (20 mg, 0.014 mmol) to give $[Ru(\mathbf{4a})_2][F_6]_6$ as a red solid (30 mg, 0.014 mmol, 99%). ^1H NMR (500 MHz, CD_3CN) δ 9.11 (s, 2H, H^{B3}), 8.72 (t, J = 8.2 Hz, 2H, H^{A3}), 8.71–8.65 (m, 6H, H^{D2+C4}), 8.24 (s, 1H, H^{C2}), 8.15 (d, J = 6.3 Hz, 4H, H^{D3}), 7.99 (t, J = 7.8 Hz, 2H, H^{A4}), 7.47 (d, J = 5.4 Hz, 2H, H^{A6}), 7.23 (t, J = 6.4 Hz, 2H, H^{A5}), 4.33 (s, 6H, H^{Me}). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ 158.8 (C^{A2}), 156.6 (C^{B2}), 153.4 (C^{A6}), 146.4 (C^{D2}), 146.3 (C^{C5}), 140.2 (C^{D4}), 139.6 (C^{B4}), 139.2 (C^{A4}), 137.8 (C^{C2}), 134.6 (C^{C4}), 130.5 (C^{D3}), 128.6 (C^{A5}), 125.6 (C^{A3}), 123.7 (C^{C1}), 122.7 (C^{B3}), 101.0 ($C^{C\text{-alkyne}}$), 87.1 ($C^{D\text{-alkyne}}$), 49.2 (Me). LR-ESI-MS found m/z 197.67 $[M - 6PF_6]^{6+}$, requires 197.39; 266.25 $[M - 5PF_6]^{5+}$ requires 265.86; 368.83 $[M - 4PF_6]^{4+}$ requires 368.57; 539.92 $[M - 3PF_6]^{3+}$ requires 539.75; 882.75 $[M - 2PF_6]^{2+}$ requires 882.11. HR-ESI-MS found 197.3940 $[M - 6PF_6]^{6+}$ requires 197.3935; 265.8653 $[M - 5PF_6]^{5+}$ requires 265.8650, 368.5725; $[M - 4PF_6]^{4+}$ requires 368.5723; 539.7514 $[M - 3PF_6]^{3+}$ requires 539.7511; 882.1099 $[M - 2PF_6]^{2+}$ requires 882.1088.

$[Ru(4b)_2](PF_6)_6$

The preparation for $[Ru(\mathbf{4b})_2](PF_6)_6$ was the same as for $[Ru(\mathbf{3b})_2](PF_6)_6$ starting from $[Ru(\mathbf{2})_2](PF_6)_2$ (20 mg, 0.016 mmol) and 1-bromododecane (3 mL, 10 mmol), to give $[Ru(\mathbf{4b})_2](PF_6)_6$ as a red solid (18 mg, 0.007 mmol, 50%). ^1H NMR (400 MHz, CD_3CN) δ 9.10 (s, 1H, H^{B3}), 8.76–8.64 (m, 4H, $H^{A3+C4+D2}$), 8.24 (s, 1H, H^{C2}), 8.16 (d, J = 6.8 Hz, 2H, H^{D3}), 7.99 (t, J = 7.9 Hz, 1H, H^{A4}), 7.47 (d, J = 5.0 Hz, 1H, H^{A6}), 7.23 (ddd, J = 7.4, 5.6, 1.1 Hz, 1H, H^{A5}), 4.53 (t, J = 7.5 Hz, 2H, H^{a}), 1.45–1.23 (m, 19H, H^{alk}), 0.88 (t, J = 6.8 Hz, 3H, H^{l}) (H^{alk} = H^{b-k}). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ 158.9 (C^{A2}), 156.7 (C^{B2}), 153.5 (C^{A6}), 146.4 (C^{C5}), 145.5 (C^{D2}), 140.5 (C^{D4}), 139.7 (C^{B4}), 139.2 (C^{A4}), 137.9 (C^{C2}), 134.7 (C^{C4}), 131.0 (C^{D3}), 128.7 (C^{A5}), 125.7 (C^{A3}), 123.8 (C^{C1}), 122.8 (C^{B3}), 101.2 ($C^{C\text{-alkyne}}$), 87.2 ($C^{D\text{-alkyne}}$), 62.8 (C^{a}), 32.6 (C^{alk}), 31.8 (C^{b}), 30.3 (C^{alk} × 2), 30.2 (C^{alk}), 30.0 (C^{alk} × 2), 29.6 (C^{alk}), 26.5 (C^{c}), 23.4 (C^{k}), 14.3 (C^{l}). LR-ESI-MS found m/z 300.10 $[M - 6PF_6]^{6+}$, requires 300.17; 389.92 $[M - 5PF_6]^{5+}$ requires 389.20; 523.08 $[M - 4PF_6]^{4+}$ requires 522.74; 746.17 $[M - 3PF_6]^{3+}$ requires 745.31; 1191.00 $[M - 2PF_6]^{2+}$ requires 1190.45. HR-ESI-MS found 300.1753 $[M - 6PF_6]^{6+}$ requires 300.1749; 389.2048 $[M - 5PF_6]^{5+}$ requires 389.2027; 522.7470 $[M - 4PF_6]^{4+}$ requires 522.7444; 745.3170 $[M - 3PF_6]^{3+}$ requires 745.3140; 1190.4540 $[M - 2PF_6]^{2+}$ requires 1190.4531.

X-Ray experimental

X-ray data were collected with ω scans to approximately 56° 2θ using a Bruker-Nonius APEX-II diffractometer employing graphite-monochromated Mo-Kα radiation generated from a sealed tube (0.71073 Å) at 293(2) K. Further experimental details including full data and details of the refinement and disorder are given in the ESI.†

Data for structure $[Ru(\mathbf{1})_2]\cdot 2PF_6\cdot 8.25H_2O$

Formula $C_{62}H_{58.50}F_{12}N_{10}O_{8.25}P_2Ru$, M 1466.70, monoclinic, space group $C2/c$(#15), a 32.008(5), b 17.136(3), c 26.226(5) Å, β 105.545(3), V 13 858(4) Å^3, D_c 1.406 g cm^{-3}, Z 8, $2\theta_{max}$ 52.74, N_{ind} 13 990(R_{merge} 0.1853), N_{obs} 6183($I > 2\sigma(I)$), N_{var} 748, residuals* $R_1(F)$ 0.0969, w$R_2(F^2)$ 0.2737, GoF(all) 0.947.

Data for structure $[Fe(1)_2]\cdot 2PF_6\cdot 6MeNO_2\cdot 12.5H_2O$

Formula $C_{68}H_{81}F_{12}FeN_{16}O_{22.50}P_2$, M 1828.28, monoclinic, space group $C2/c$(#15), a 31.977(4), b 16.992(2), c 26.943(3) Å, β 106.844(2), V 14 011(3) Å^3, D_c 1.733 g cm^{-3}, Z 8, $2\theta_{max}$ 52.74, N_{ind} 14 269(R_{merge} 0.0957), N_{obs} 6998($I > 2\sigma(I)$), N_{var} 788, residuals $R_1(F)$ 0.0969, w$R_2(F^2)$ 0.3026, GoF(all) 0.964.

Data for structure $3[Ru(1)_2]\cdot 5PF_6\cdot NO_3$

Formula $C_{186}H_{126}F_{30}N_{31}O_3P_5Ru_3$, M 3871.24, triclinic, space group $P\bar{1}$(#2), a 19.323(5), b 20.548(6), c 26.542(7) Å, α 81.138(5), β 81.923(5), γ 84.253(5)°, V 10 276(5) Å^3, D_c 1.251 g cm^{-3}, Z 2, $2\theta_{max}$ 49.74, N 34 434, N_{obs} 14 864($I > 2\sigma(I)$), N_{var} 1616, residuals $R(F^2)$ 0.1271, $R_w(F^2)$ 0.3249, GoF(all) 1.138.

Data for structure $[Ru(2)_2](PF_6)_2\cdot 4Et_2O$

Formula $C_{86}H_{82}F_{12}N_{10}O_4P_2Ru$, M 1710.63, orthorhombic, space group $Fddd$(#70), a 21.841(3), b 25.024(2), c 34.582(3) Å, V 18 900(4) Å^3, D_c 1.202 g cm^{-3}, Z 8, $2\theta_{max}$ 52.00, N 37 508, N_{ind} 4660(R_{merge} 0.0978), N_{obs} 2980($I > 2\sigma(I)$), N_{var} 312, residuals $R(F^2)$ 0.0537, $R_w(F^2)$ 0.1111, GoF(all) 1.053.

Results and discussion

Ligand synthesis

Ligands **1** and **2** were prepared from 4′-(3,5-dibromophenyl)-2,2′:6′:2″-terpyridine (**5**)[21] using palladium(0)-catalysed coupling reactions, as shown in Scheme 1. The reaction of **5** with an excess (3 equiv.) of 4-pyridineboronic acid pinacol ester,[25] 20 mol% $Pd(PPh_3)_4$, 10 equiv. $CsCO_3$ in degassed DMF gave ligand **1** in 85% yield after purification. Copper-free palladium(0)-catalysed Sonogashira coupling of **5** with 3 equiv. of freshly deprotected 4-ethynylpyridine,[22] 20 mol% $Pd(PPh_3)_4$ THF–diethylamine gave ligand **2** in 84% isolated yield. The use of other common solvents gave reproducibly lower yields, for example toluene–NEt_3: 40%; DMF–DME–NEt_3: <5%. The addition of copper(I) to the reaction mixtures were also found to significantly lower yields (*e.g.* the use of 30 mol% CuI gave a 65% yield of **5** under otherwise identical conditions).

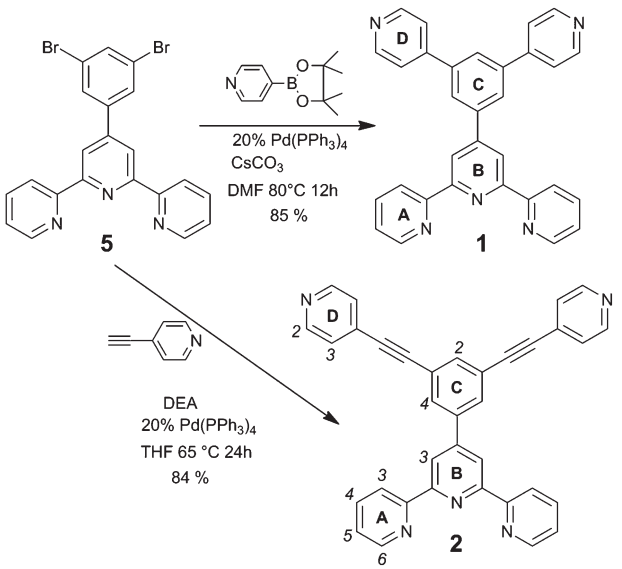
The ^{1}H and ^{13}C NMR data for ligands **1** and **2** are typical for 4′-substituted terpyridine complexes, and were unambiguously assigned using 1D and 2D (COSY, HSQC, HMBC) techniques (see Experimental section for assignments).

Fe(II) and Ru(II) complex synthesis and characterisation

The very high thermodynamic stability of $[Fe(tpy)_2]^{2+}$ complexes and their relatively labile nature drives the selective formation the desired $[FeL_2]^{2+}$ complexes in near quantitative isolated yields under ambient conditions, as is typical for $[Fe(tpy)_2]^{2+}$ complexes. Reaction of two equivalents of ligand **1** with $FeCl_2\cdot 4H_2O$ in ethanol at room temperature for 30 min, followed by anion exchange with excess aqueous NH_4PF_6, gave pure $[Fe(1)_2](PF_6)_2$ in 90% yield. The analogous complex $[Fe(2)_2](PF_6)_2$ was prepared in similar yield. The ^{1}H NMR spectra (CD_3CN) of these complexes, shown in Fig. 2, reveals the expected 4-fold symmetry of the complex, with the same pattern of signals as observed for the free ligands.

The signals of the tpy protons are essentially identical in the two complexes, with the notable exception of the signal of H^{B3} which is shifted from 9.38 to 9.26 ppm on introduction of the alkyne spacer, although the corresponding values for the free ligands [$CDCl_3$ 8.81 (**1**); 8.76 ppm (**2**)] are more similar. The expected differences for the signals of the pendant phenyl ring protons are observed, for example with signal H^{C2} being shifted upfield from 8.39 to 8.15 ppm on introduction of the alkyne spacer, and the corresponding ^{13}C NMR signal (C^{C2}) is shifted from 128.8 to 137.0 ppm. However, the ^{13}C NMR signal for the C^{C5} carbon, which is the attachment point to the tpy unit, is virtually unchanged in the two complexes (150.3 and 149.1), and the C^{B4} (139.6 and 139.0 ppm) is similarly insensitive to the substitution difference, hinting to minimal electronic interaction with the tpy unit. Electrospray Ionisation Mass Spectrometry (ESI-MS) was used to confirm the identity of the complexes, with peaks corresponding to $[Fe(L)_2]^{2+}$ and $[Fe(L)_2](PF_6)^+$ matching the calculated isotope patterns for these species; High resolution ESI-MS unambiguously established molecular composition (*e.g.* for $[Fe(1)_2](PF_6)_2$: 491.1492 $[M - 2PF_6]^{2+}$ requires 491.1495 m/z).

Attempts to prepare the corresponding Ru(II) complexes, $[Ru(1)_2](PF_6)_2$ and $[Ru(2)_2](PF_6)_2$, using standard reaction



Scheme 1 Synthesis of **1** and **2**, with atom labelling shown. See Experimental section for details.

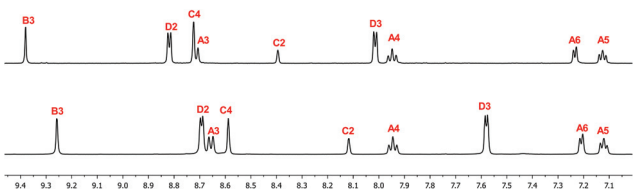
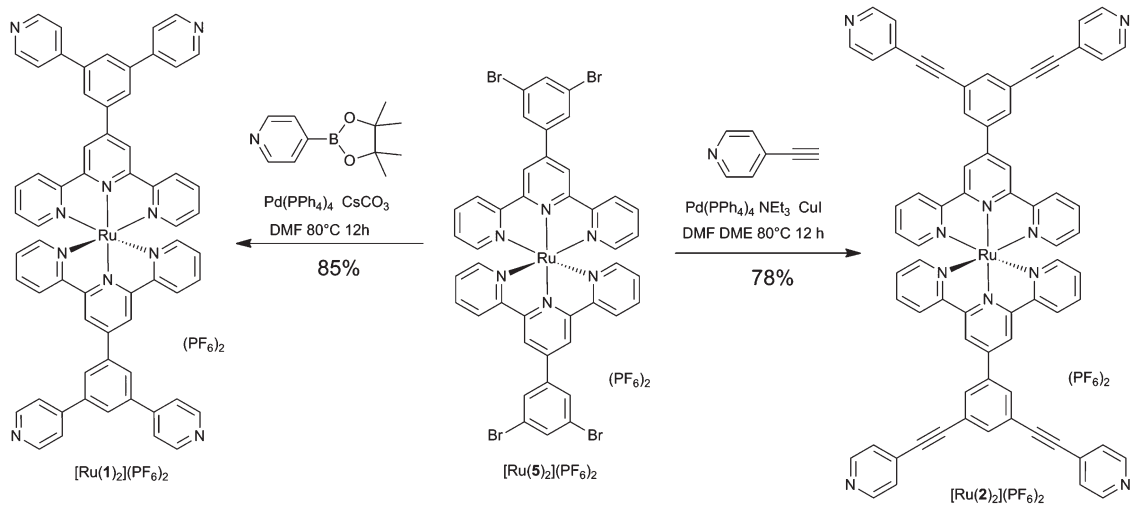


Fig. 2 ^{1}H NMR (CD_3CN, 500 MHz) of $[Fe(1)_2](PF_6)_2$ (top) and $[Fe(2)_2](PF_6)_2$ (bottom). See Fig. 1 for atom labelling.



Scheme 2 Synthesis of Ru(II) complexes of ligands **1** and **2** *via* Pd(0) coupling reactions on $[Ru(\mathbf{5})_2](PF_6)_2$.

conditions ($RuCl_3{\cdot}xH_2O$ in using refluxing ethanol;[26] or $Ru(DMSO)_4Cl_2$ in ethylene glycol under microwave irradiation[27]) gave very poor yields of the desired complexes, presumably as the result of kinetically controlled polymer formation due to the more inert nature of Ru(II) with respect to Fe(II). To overcome this problem, the Ru(II) complex of the parent dibromo ligand, $[Ru(\mathbf{5})_2](PF_6)_2$ [28,29] was prepared using standard microwave conditions[27] in 90% yield after purification (Scheme 2). Palladium(0)-mediated couplings on $[Ru(4'\text{-}(4\text{-bromophenyl})\text{-tpy})_2](PF_6)_2$ and related boronic acids/esters,[18b] has been previously established, and here we demonstrate direct coupling on $[Ru(\mathbf{5})_2](PF_6)_2$ is an effective method to directly introduce multiple substituents on to Ru(II) polypyridyl complexes in high yields. The four-fold Suzuki coupling of $[Ru(\mathbf{5})_2](PF_6)_2$ with excess 4-pyridineboronic acid pinacol ester (DMF, $CsCO_3$, 20 mol% $Pd(PPh_3)_4$ for 12 h at 80 °C gave $[Ru(\mathbf{1})_2](PF_6)_2$ in an excellent 85% yield after column chromatography. Similarly, the coupling with 4-ethynylpyridine (DMF–DME, 40 mol% $Pd(PPh_3)_4$, 40 mol% CuI) for 12 h at 80 °C gave $[Ru(\mathbf{2})_2](PF_6)_2$ in 78% isolated yield.[30] The significance of this synthetic approach is the ease of work-up: the use of a relatively high catalyst loading (10% per reaction site) and an excess of pyridine-coupling components lead to a negligible impurity of Ru(II) complexes, which makes isolation of the charged and coloured complex from organic impurities, such as homo-coupled alkynes, very straightforward. A comparison of the ^{1}H NMR spectra of $[Ru(\mathbf{1})_2](PF_6)_2$ and $[Ru(\mathbf{2})_2](PF_6)_2$ (Fig. 3) demonstrates the same trend as the corresponding Fe(II) complexes, with typical peak shifts associated with the shorter M–N bond length of Ru(II) complexes relative to their Fe(II) analogues. High resolution ESI-MS confirmed molecular composition for both complexes (see ESI† for details).

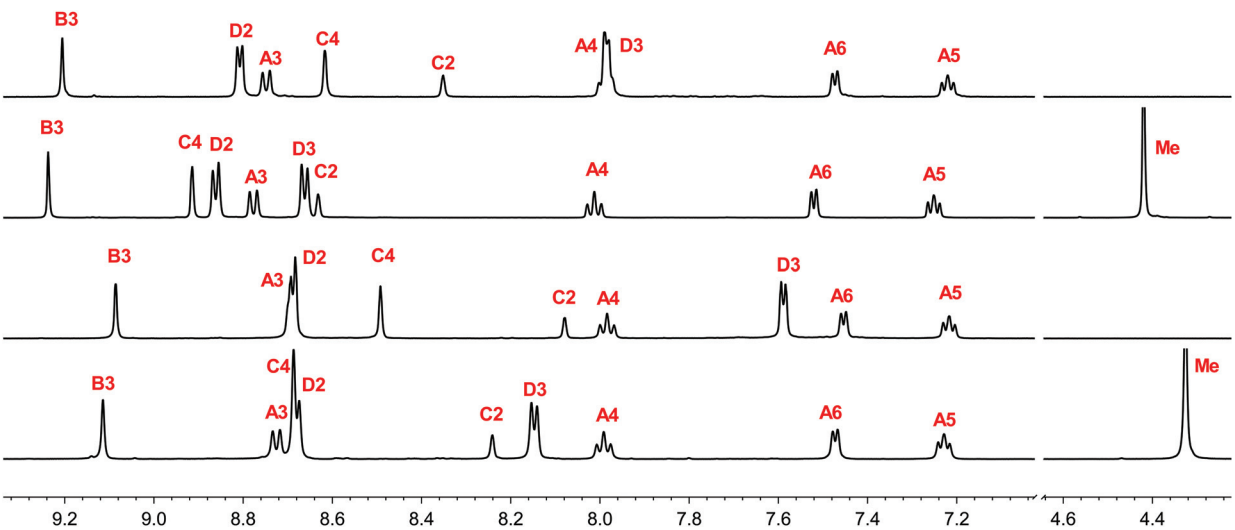


Fig. 3 ^{1}H NMR (CD_3CN, 500 MHz) of Ru(II) complexes: (top to bottom) $[Ru(\mathbf{1})_2](PF_6)_6$; $[Ru(\mathbf{3a})_2](PF_6)_6$; $[Ru(\mathbf{2})_2](PF_6)_6$ and $[Ru(\mathbf{4a})_2](PF_6)_6$. See Fig. 1 for atom labelling.

X-Ray crystal structures†

Single crystals of $[Fe(\mathbf{1})_2](PF_6)_2{\cdot}6MeNO_2{\cdot}12.5H_2O$ and $[Ru(\mathbf{1})_2](PF_6)_2{\cdot}8.25H_2O$ were grown by slow evaporation of nitromethane–acetonitrile or toluene–acetonitrile solutions of the complexes respectively. The structures are isomorphous, crystallise in the C_2/c space group, contain a single complex in the asymmetric unit with disordered solvent (modelled as water molecules) and only one of the two PF_6 anions is ordered. The structure of $[Fe(\mathbf{1})_2]^{2+}$ is shown in Fig. 4, and shows the expected octahedral coordination of the metal centre and the orthogonal orientation of the two tpy groups, with the angle between the least-squares-planes of the tpy groups being 86.64°.

Intermolecular crystal packing is dominated by extensive π–π stacking, including the type of tpy–tpy embraces commonly observed for $\{M(tpy)_2\}^{n+}$ complexes.[31] The terminal pyridine rings of the tpy units are weakly associated by favourable off-set face-to-face stacking and edge-to-face interactions with similar groups of adjacent complexes (Fig. 5a). Both of the pendant (3,5-pyridyl)phenyl groups are efficiently packed together supported by close packing interactions to form columns of four complexes (related by an inversion centre) sandwiched between $M(tpy)_2$ units (Fig. 5b). The closest interactions are between phenyl and pendant pyridine groups and the four-molecule-stack is based on this complementary repeat unit. Finally, the lattice contains a large volume of void space, which is filled with disordered solvent and anion molecules.

When diethyl ether was slowly diffused into a DMF solution of $[Ru(\mathbf{1})_2](PF_6)_2$ and KNO_3 a different crystal form ($3[Ru(\mathbf{1})_2]{\cdot}5PF_6{\cdot}NO_3$, space group $P\bar{1}$) was obtained, shown in Fig. 6, which contained three structurally similar but crystallographically independent Ru(II) complexes. In each case the pendant pyridine groups of each end are approximately coplanar, a likely consequence of crystal packing. The self-complementary shape of the complex allows effective packing to form 2D sheets very different to the previous structure. Although extensive π–π stacking is apparent, the interactions are relatively weak, with

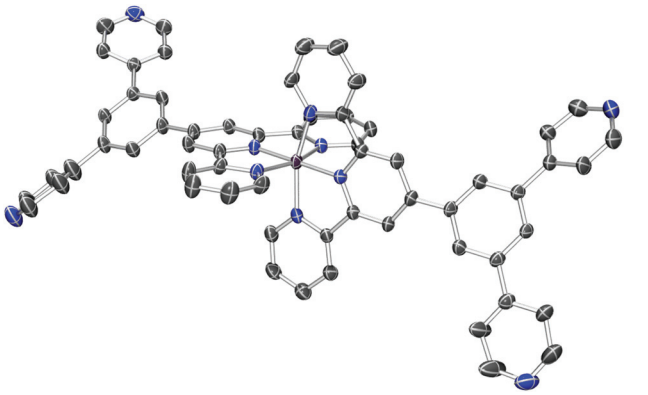


Fig. 4 X-ray crystal structure of $[Fe(\mathbf{1})_2]^{2+}$ in $[Fe(\mathbf{1})_2](PF_6)_2{\cdot}6MeNO_2{\cdot}12.5H_2O$. Hydrogen atoms, anions and solvent omitted for clarity, thermal ellipsoids are drawn to 30% probability.

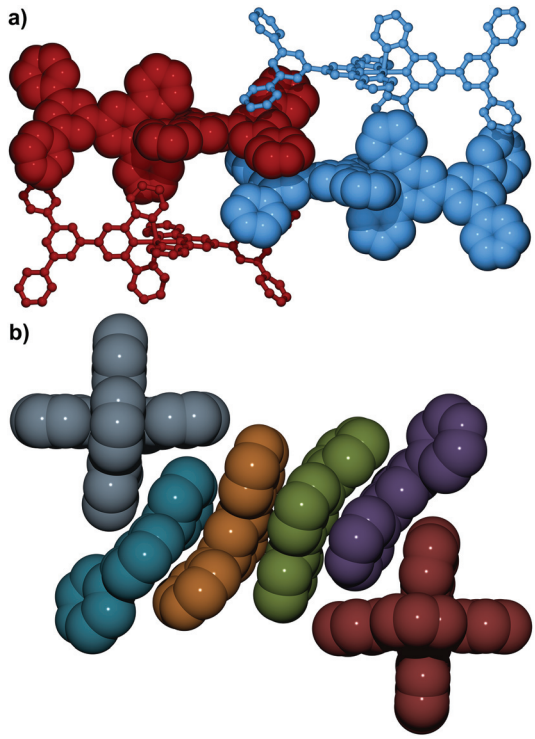


Fig. 5 Crystal packing for $[Fe(\mathbf{1})_2]^{2+}$ in $[Fe(\mathbf{1})_2](PF_6)_2{\cdot}6MeNO_2{\cdot}12.5H_2O$. All molecules crystallographically equivalent. Hydrogen atoms, solvent and anions are omitted for clarity. (a) Showing the overall packing of the complexes with py_{tpy} to py_{tpy} centroid to least-squares-plane of ring of 3.651 Å (i = 1.5 − x, −1/2 + y, 1.5 − z). Distances from the centroid of the phenyl rings to least-squares plane of $py_{pendant}$ of adjacent i complex are 3.621 Å (i = 1 − x, 1 − y, 1 − z) and 3.458 Å (i = −1/2 + x, 1.5 − y, −1/2 + z. (b) Stacks of four complexes are sandwiched between $\{M(tpy)_2\}$ units to highlight packing arrangement. For the end complexes, only the tpy units are shown, for the middle complexes only the 4′-pendant groups are shown.

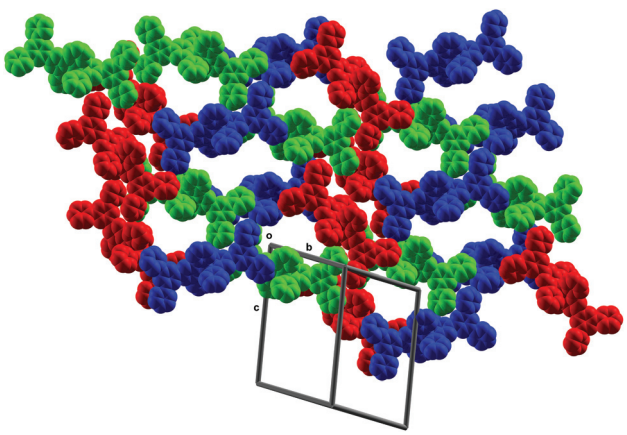


Fig. 6 Crystal packing for $[Ru(\mathbf{1})_2]^{2+}$ in $3[Ru(\mathbf{1})_2]{\cdot}5PF_6{\cdot}NO_3$. Molecules are coloured by symmetry equivalence; unit cell shown in grey. Example tpy–tpy embrace: the distance from the centroid of the tpy pyridine ring containing N3 to the plane formed the ring containing N17 is 3.396 Å. Void space is occupied by badly disordered solvent and anions which are omitted for clarity. Two pendant pyridine rings are disordered over two positions each (only one position shown of each).

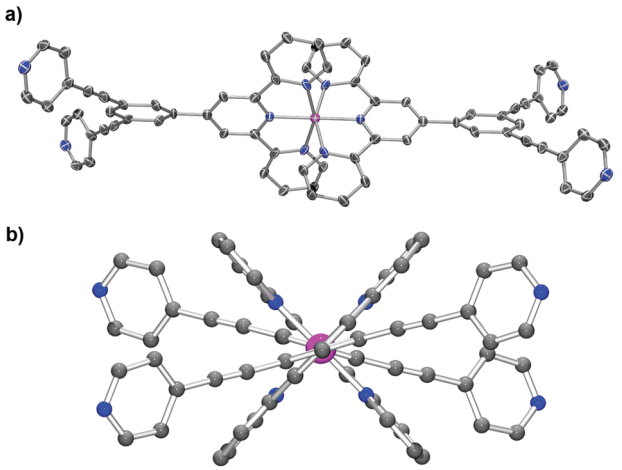


Fig. 7 Structure of $[Ru(\mathbf{2})_2]^{2+}$ in $[Ru(\mathbf{2})_2](PF_6)_2{\cdot}4Et_2O$ with hydrogen atoms, and anions omitted for clarity. (a) ORTEP representation (ellipsoids drawn at 30% probability) from the side and (b) ball-and-stick view from the end of the molecule. The angle between the least-squares-planes formed by the pendant nitrogens and the phenyl rings of each end of the complex is 30.0°; the alkyne C≡C bond length is 1.158(4) Å and Ru–N bonds are 1.998(3) and 2.085(2) Å; the angle between the least-squares planes of the tpy groups is 86.05°.

most contacts being the result of weak van der Waals interactions rather than any specific or directional interactions.

Single crystals of $[Ru(\mathbf{2})_2](PF_6)_2{\cdot}4Et_2O$ were grown by vapour diffusion of diethylether into a nitrobenzene–nitromethane solution of the complex. The structure, shown in Fig. 7, crystallises in the orthorhombic space group *Fddd* with the Ru atom located on a fourfold special position resulting in 1/4 of a complex in the asymmetric unit. The complexes are packed to form 2D sheets (Fig. 8) *via* close stacking between the pendant arms of adjacent complexes and voids are occupied by solvent and anions, with short non-classical CH···F hydrogen bonds

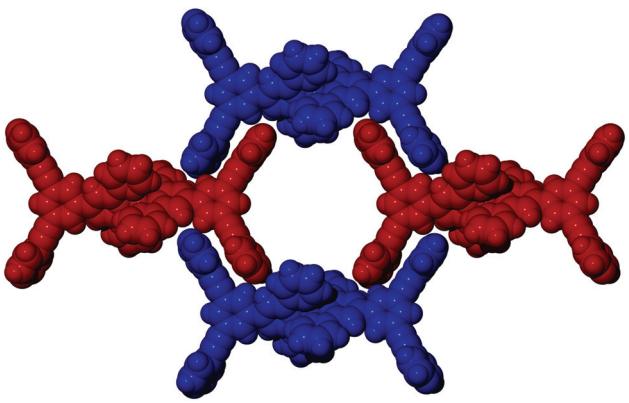


Fig. 8 Packing for $[Ru(\mathbf{2})_2]^{2+}$ in $[Ru(\mathbf{2})_2](PF_6)_2{\cdot}4Et_2O$, with anions and solvent omitted for clarity. All molecules crystallographically equivalent. End-to-face aromatic contacts from the tpy pyridine of C(12)···H(3)i–C(3)i = 3.002; C(11)···H(2)ii–C(2)i 3.030 Å (i = 2 − *x*, 1/4 + *y*, 1/4 + *z*). Close contacts with diethyl ether solvent molecules, and non-classical hydrogen bonds from between a PF_6 anion and the protons of the tpy ring, *e.g.* [H(1) to F(1)i (i = 1.5 − *x*, −1/4 + *y*, −3/4 + *z*) = 2.437; H(1) to F(3)ii (ii = 1/2 + *x*, 1/4 − *y*, 3/4 − *z*) = 2.599; H(2) to F(2)iii (iii = 1/2 + *x*, 1/4 − *y*, 3/4 − *z*) = 2.447 Å] and the pendant pyridine [H(17) to F(1)iv (iv = 1/4 + *x*, 1/2 − *y*, −1/4 + *z*) = 2.563 Å].

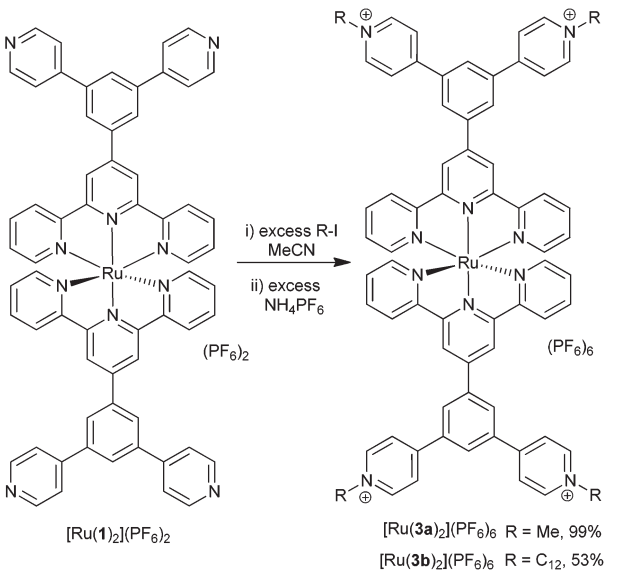
formed between tpy CH groups and PF_6^- anions (see Fig. 8 caption for details).

N-Alkylation of Ru(II) complexes

The reactivity of the pendant pyridyl towards alkylating agents was examined as a ready method for introducing additional functional or binding groups (Scheme 3), an approach which has been previously used for building pyridyl-functionalised complexes into larger assemblies.[32] The reaction of $[Ru(\mathbf{1})_2](PF_6)_2$ with excess methyl iodide in refluxing acetonitrile with added NH_4PF_6 (to prevent precipitation of the complex as the iodide salt)[33] for 12 h gave the tetra-alkylated product $[Ru(\mathbf{3a})_2](PF_6)_6$ in quantitative yield following a straightforward workup. The reaction of $[Ru(\mathbf{1})_2](PF_6)_2$ with iodododecane proceeds similarly to give $[Ru(\mathbf{3b})_2](PF_6)_6$ in 53% yield.

The reaction of the analogous complex with an alkyne spacer, $[Ru(\mathbf{2})_2](PF_6)_2$ with methyl iodide gave $[Ru(\mathbf{4a})_2](PF_6)_6$ in quantitative yield. The reaction of $[Ru(\mathbf{2})_2](PF_6)_2$ with bromododecane similarly gave $[Ru(\mathbf{4b})_2](PF_6)_6$ in 50% yield. In each case ESI-MS confirmed the identity of the complexes, with peaks corresponding to sequential loss of PF_6 counter ions which matched the calculated isotope patterns for these 6+, 5+, 4+, 3+, 2+ species (see ESI† for details).

A comparison of the ^1H NMR spectra (CD_3CN) of $[Ru(\mathbf{3a})_2]^{6+}$ and $[Ru(\mathbf{4a})_2]^{6+}$ with their non-alkylated parent complexes (Fig. 3) shows the pendant pyridyl signals are shifted in accord with the alkylation of the nitrogen group with the H^{D3} signals shifted downfield by 0.68 and 0.56 ppm for $[Ru(\mathbf{3a})_2](PF_6)_6$ and $[Ru(\mathbf{4a})_2](PF_6)_6$ respectively. The appearance of a new signal at 4.42 ppm for $[Ru(\mathbf{3a})_2](PF_6)_6$ and 4.33 ppm for $[Ru(\mathbf{4a})_2](PF_6)_6$, corresponds to the *N*-methyl group. Importantly, signals of the tpy unit were essentially unchanged by the alkylation despite the introduction of an additional 4+ charge to the complex. Complexes $[Ru(\mathbf{3b})_2]^{6+}$ and $[Ru(\mathbf{4b})_2]^{6+}$ exhibit excellent solubility in organic solvents such as THF



Scheme 3 Synthesis of *N*-alkyl derivatives of $[Ru(\mathbf{1})_2](PF_6)_2$.

and dichloromethane despite their high charge, as might be expected given the dodecyl chains. Preliminary studies of binding of pillar[n]arene macrocycles[34] by these complexes revealed only very weak association (see ESI† for details), eliminating the possibility of these groups as viable recognition elements.

Spectroscopic and electrochemical studies

The UV-visible absorption spectrum of each complex was recorded in acetonitrile. All Fe(II) and Ru(II) complexes exhibited typical MLCT absorptions around 570 and 490 nm respectively, unshifted from the corresponding parent 4′-phenylterpyridine complexes (Fig. 9 and Table S1†). The series of π* ← π transitions are dominated by those of the tpy unit and also correspond closely with those of the parent phenyl-tpy complexes.[35] As may be expected, the introduction of pyridyl substituents generates additional π* ← π transitions with marked increased absorption (by 40% at ~254 nm) on introduction of the additional conjugation of the alkyne spacer. The alkylation of the Ru(II) complexes produced an increase in the intensity of the MLCT transition but no change in the energy, in addition to expected increases in the intensity of the ligand-centred transitions.

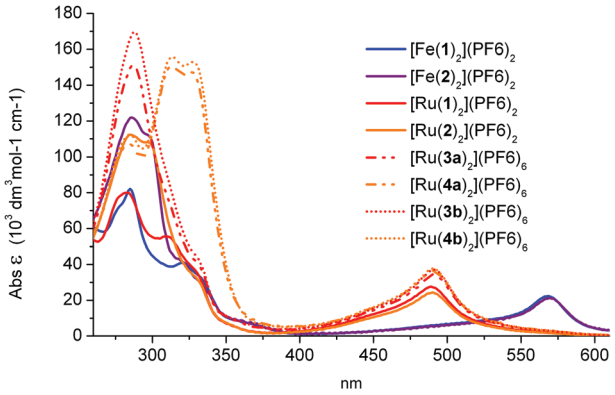


Fig. 9 Absorption spectra (CH_3CN) of complexes $[Fe(\mathbf{1})_2](PF_6)_2$, $[Fe(\mathbf{2})_2](PF_6)_2$, $[Ru(\mathbf{1})_2](PF_6)_2$, $[Ru(\mathbf{2})_2](PF_6)_2$, $[Ru(\mathbf{3a})_2](PF_6)_6$, $[Ru(\mathbf{3b})_2](PF_6)_6$, $[Ru(\mathbf{4a})_2](PF_6)_6$, $[Ru(\mathbf{4b})_2](PF_6)_6$.

Cyclic voltammetry (CV) measurements (Table 1, Fig. S43–S50 and Table S2†) show $M^{2+/3+}$ redox potentials unshifted from the parent 4′-phenyl-tpy (Phtpy) complexes. For example, +0.72 (*vs.* Fc/Fc^+) and +0.89 V for $[Fe(\mathbf{1})_2](PF_6)_2$ and $[Ru(\mathbf{1})_2](PF_6)_2$ compared with +0.69 V and +0.90 for the respective Phtpy complexes. At negative potentials both the Fe(II) and Ru(II) complexes of ligand **2** were found to readily absorb onto the glassy carbon electrode, with $[Fe(\mathbf{2})_2](PF_6)_2$ reproducibly producing a sharp desorption peak at −1.45 V during the return wave (see Fig. S44†). Careful investigation established this was the result of an irreversible process at −1.63 V.

The $Ru^{2+/3+}$ redox potential was similarly unaffected by alkylation of the pendant pyridine groups despite the additional charge introduced on the complex. However, the introduction of an addition 4+ charge onto the complex provided ample capacity for multiple-electron reduction processes. Several reversible, and several irreversible processes occur, but the type of absorption onto the electrode observed for the free pyridine units was not observed. Differential Pulse Voltammetry (DPV) was used to confirm these processes involved up to six electrons each (see ESI† for data).

Interactions with metal centres

The pendant pyridyl groups of complexes $[Ru(\mathbf{1})_2](PF_6)_2$ and $[Ru(\mathbf{2})_2](PF_6)_2$ are well-suited for coordinating to metal centres for the formation of coordination networks or discrete assemblies. In order to investigate the reactivity of these groups towards metal centres we chose the common Zn(II) tetraphenylporphyrin (Zntpp) as a model complex as it is known to bind to single pyridine groups,[38] is diamagnetic (allowing standard NMR techniques) and is kinetically stable to demetallation. The reaction of 4 equivalents of Zntpp with 1 equivalent of $[Ru(\mathbf{1})_2](PF_6)_2$ or $[Ru(\mathbf{2})_2](PF_6)_2$ results in the spontaneous assembly of the 5-component assembly shown in Fig. 10. ESI-MS confirmed the composition of the assembly, with peaks corresponding to 1–4 molecules of Zntpp coordinated to the complex (Fig. 11).

Table 1 Redox potentials for $[ML_2](PF_6)_2$ (M = Fe, Ru; L = **1**, **2**, **3**, **4**, **5**, **6**).[a] Data for $[Ru(tpy)_2]^{2+}$ and $[Ru(Phtpy)_2]^{2+}$ are from ref. 36

	$M^{2+/3+}$	Ligand reductions			
$[Fe(tpy)_2](PF_6)_2$[32b]	+0.74		−1.64		−1.82
$[Fe(Phtpy)_2](PF_6)_2$	+0.69		−1.62	−1.73	−2.34
$[Fe(\mathbf{1})_2](PF_6)_2$	+0.72		−1.57	−1.68	−2.25
$[Fe(\mathbf{2})_2](PF_6)_2$	+0.73	-1.51^{qr}	$-1.54^{red}/-1.45^{abs/reox}$	$-1.63^{red}/-1.53^{reox}$	-1.58^{qr}
$[Ru(tpy)_2](PF_6)_2$[36]	+0.92		−1.67		−1.92
$[Ru(Phtpy)_2](PF_6)_2$[36,37]	+0.90		−1.66		1.92
$[Ru(\mathbf{1})_2](PF_6)_2$	+0.89		−1.60	−1.84	−2.26
$[Ru(\mathbf{2})_2](PF_6)_2$	+0.91	−1.55	-1.56^{abs}	-1.63^{reox}	-1.77^{qr}
$[Ru(\mathbf{3a})_2](PF_6)_6$	+0.89	-1.20^{abs}	−1.42	−1.54	−1.83
				-1.66^{qr}	-2.28^{irr}
$[Ru(\mathbf{3b})_2](PF_6)_6$	+0.89		−1.40	-1.61^{qr}	−1.77
$[Ru(\mathbf{4a})_2](PF_6)_6$[b]	+0.89	-1.26^{irr}	$-1.67^{qr\,b}$	-1.89^{irr}	-2.35^{irr}
$[Ru(\mathbf{4b})_2](PF_6)_6$	+0.90	-1.24^{irr}	-1.51^{irr}	-1.54^{qr}	-1.78^{qr}

[a] All measurements in MeCN with 0.1 M $[n\text{BuN}]PF_6$, with a glassy carbon working electrode, platinum counter electrode, $Ag^+/AgCl$ reference and potentials quoted are *versus* Fc^+/Fc. All processes are reversibly, except where noted qr = quasi-reversible (reduction peak given), irr = irreversible. Phtpy = 4′-phenyl-2,2′:6′,2″-terpyridine. [b] Several additional irreversible processes also between −1.5 to −1.9 V.

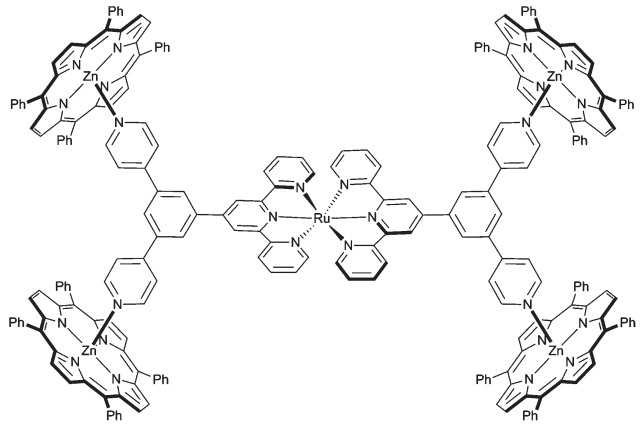


Fig. 10 $[Ru(\mathbf{1})_2]^{2+}$ binding four Zntpp molecules.

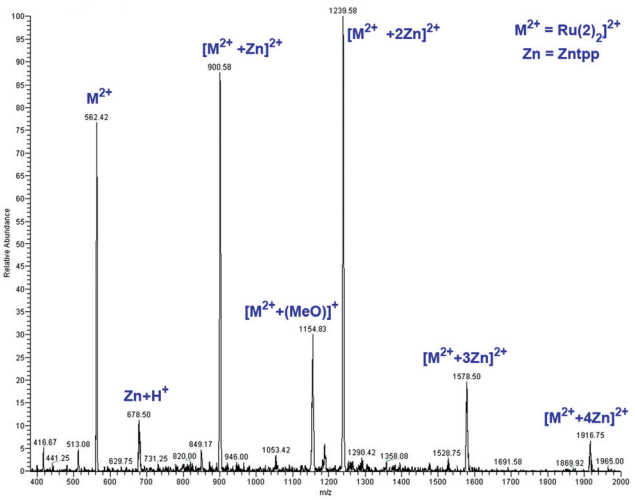


Fig. 11 ESI-MS of $Ru(\mathbf{2})_2(PF_6)_2$ with Zn(II) tetraphenylporphyrin (Zntpp).

The association constants between Zntpp and $[Ru(\mathbf{1})_2]^{2+}$ and $[Ru(\mathbf{2})_2]^{2+}$ were determined by NMR titrations ($CDCl_3$–CD_3CN 2 : 1) by assuming each binding site is unique and that the effective "pyridine" concentration of four times the Ru concentration.[39] Fitting[40] of the obtained data found pseudo association constants of 660 ± 40 M^{-1} and 920 ± 70 M^{-1} for and $[Ru(\mathbf{1})_2]^{2+}$ and $[Ru(\mathbf{2})_2]^{2+}$ and respectively, comparable with typical Zntpp binding with pyridine in a competitive solvent (acetonitrile).[41] This confirms the potential of complexes $[Ru(\mathbf{1})_2]^{2+}$ and $[Ru(\mathbf{2})_2]^{2+}$ for bridging multiple metal centres. The use of extended systems of this type for templating the formation of porphyrin nanorings has been explored by the Anderson group,[42] and a similar approach using complexes of the type $[Ru(\mathbf{1})_2]^{2+}$ and $[Ru(\mathbf{2})_2]^{2+}$ may also be possible.

Conclusions

Using an easily prepared $Ru(tpy)_2^{2+}$ complex, we have demonstrated 4-fold Suzuki and Sonogashira coupling reactions can be readily performed on the complex in good yields and with straightforward purification. The multi-pyridine decorated complexes formed were shown to be reactive towards alkylating agents and metal ions and show promise for incorporation into larger supramolecular assemblies and networks. The absorption and redox properties were investigated and both found to be largely unaffected from the parent 4′-phenyltpy complexes.

Notes and references

1 (*a*) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi and M. Fujita, *Science*, 2010, **328**, 1144–1147; (*b*) Y. Inokuma, M. Kawano and M. Fujita, *Nat. Chem.*, 2011, **3**, 349–358; (*c*) C. R. K. Glasson, J. K. Clegg, J. C. McMurtrie, G. V. Meehan, L. F. Lindoy, C. A. Motti, B. Moubaraki, K. S. Murray and J. D. Cashion, *Chem. Sci.*, 2011, **2**, 540–543.

2 C. Piguet, M. Borkovec, J. Hamacek and K. Zeckert, *Coord. Chem. Rev.*, 2005, **249**, 705–726.

3 (*a*) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson and F. Huang, *Angew. Chem., Int. Ed.*, 2010, **49**, 1090–1094; (*b*) G. R. Whittell, M. D. Hager, U. S. Schubert and I. Manners, *Nat. Mater.*, 2011, **10**, 176–188.

4 (*a*) H. W. Roesky and M. Andruh, *Coord. Chem. Rev.*, 2003, **236**, 91–119; (*b*) I. Eryazici, O. K. Farha, O. C. Compton, C. Stern, J. T. Hupp and S. T. Nguyen, *Dalton Trans.*, 2011, **40**, 9189–9193.

5 A. Schultz, X. Li, B. Barkakaty, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2012, **134**, 7672–7675.

6 Z. J. Wang, K. N. Clary, R. G. Bergman, K. N. Raymond and F. D. Toste, *Nat. Chem.*, 2013, **5**, 100–103.

7 E. C. Constable, *Coord. Chem. Rev.*, 2008, **252**, 842–855.

8 A. M. Shultz, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2009, **131**, 4204–4205.

9 M.-P. Santoni, G. S. Hanan, B. Hasenknopf, A. Proust, F. Nastasi, S. Serroni and S. Campagna, *Chem. Commun.*, 2011, **47**, 3586–3588.

10 For examples, see: (*a*) M. Schwalbe, M. Karnahl, H. Görls, D. Chartrand, F. Laverdiere, G. S. Hanan, S. Tschierlei, B. Dietzek, M. Schmitt, J. Popp, J. G. Vos and S. Rau, *Dalton Trans.*, 2009, 4012–4022; (*b*) I. Tomatsu, K. Peng and A. Kros, *Adv. Drug Delivery Rev.*, 2011, **63**, 1257–1266; (*c*) G. Dehaen, S. V. Eliseeva, P. Verwilst, S. Laurent, L. Vander Elst, R. N. Muller, W. De Borggraeve, K. Binnemans and T. N. Parac-Vogt, *Inorg. Chem.*, 2012, **51**, 8775–8783; (*d*) C. R. K. Glasson, W. Song, D. L. Ashford, A. Vannucci, Z. Chen, J. J. Concepcion, P. L. Holland and T. J. Meyer, *Inorg. Chem.*, 2012, **51**, 8637–8639; (*e*) Y. Hao, P. Yang, S. Li, X. Huang, X.-J. Yang and B. Wu, *Dalton Trans.*, 2012, **41**, 7689–7694; (*f*) A. Baron, C. Herrero, A. Quaranta, M.-F. Charlot, W. Leibl, B. Vauzeilles and A. Aukauloo, *Inorg. Chem.*, 2012, **51**, 5985–5987.

11 For examples, see: (*a*) F. R. Keene, *Dalton Trans.*, 2011, **40**, 2405–2418; (*b*) H. Song, J. T. Kaiser and J. K. Barton, *Nat. Chem.*, 2012, **4**, 615–620; (*c*) B. S. Howerton, D. K. Heidary and E. C. Glazer, *J. Am. Chem. Soc.*, 2012, **134**, 8324–8327.
12 For examples, see: (*a*) R. Shunmugam, G. J. Gabriel, K. A. Aamer and G. N. Tew, *Macromol. Rapid Commun.*, 2010, **31**, 784–793; (*b*) G. Gröger, W. Meyer-Zaika, C. Böttcher, F. Gröhn, C. Ruthard and C. Schmuck, *J. Am. Chem. Soc.*, 2011, **133**, 8961–8971; (*c*) R. Siebert, A. Winter, M. Schmitt, J. Popp, U. S. Schubert and B. Dietzek, *Macromol. Rapid Commun.*, 2012, **33**, 481–497.
13 For examples, see: (*a*) J. E. Beves, E. C. Constable, C. E. Housecroft, C. J. Kepert and D. J. Price, *CrystEngComm*, 2007, **9**, 456–459; (*b*) J. E. Beves, E. C. Constable, S. Decurtins, E. L. Dunphy, C. E. Housecroft, T. D. Keene, M. Neuburger and S. Schaffner, *CrystEngComm*, 2008, **10**, 986–990; (*c*) J. E. Beves, D. J. Bray, J. K. Clegg, E. C. Constable, C. E. Housecroft, K. A. Jolliffe, C. J. Kepert, L. F. Lindoy, M. Neuburger, D. J. Price, S. Schaffner and F. Schaper, *Inorg. Chim. Acta*, 2008, **361**, 2582–2590.
14 For a review, see: V. Balzani, G. Bergamini, F. Marchioni and P. Ceroni, *Coord. Chem. Rev.*, 2006, **250**, 1254–1266.
15 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483.
16 R. Chinchilla and C. Nájera, *Chem. Rev.*, 2007, **107**, 874–922.
17 For examples of Suzuki coupling on tpy derivatives see: (*a*) M. Kimura, T. Shiba, T. Muto, K. Hanabusa and H. Shirai, *Chem. Commun.*, 2000, 11–12; (*b*) W. Goodall, K. Wild, K. J. Arm and J. A. G. Williams, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1669–1681; (*c*) F. S. Han, M. Higuchi and D. G. Kurth, *Org. Lett.*, 2007, **9**, 559–562; (*d*) A. D'Aléo, E. Cecchetto, L. De Cola and R. Williams, *Sensors*, 2009, **9**, 3604–3362; (*e*) M. Schwalbe, R. Metzinger, T. S. Teets and D. G. Nocera, *Chem.–Eur. J.*, 2012, **18**, 15449–15458; For Suzuki coupling on related polypyridines, see: (*f*) B. Schlicke, P. Belser, L. De Cola, E. Sabbioni and V. Balzani, *J. Am. Chem. Soc.*, 1999, **121**, 4207–4214; (*g*) J. Hankache and O. S. Wenger, *Chem. Commun.*, 2011, **47**, 10145–10147; (*h*) A. M. Bünzli, H. J. Bolink, E. C. Constable, C. E. Housecroft, M. Neuburger, E. Ortí, A. Pertegás and J. A. Zampese, *Eur. J. Inorg. Chem.*, 2012, 3780–3788.
18 For Suzuki coupling on Ru(II) complexes, see: (*a*) C. Patoux, J.-P. Launay, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin, S. James and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1998, **120**, 3717–3725; (*b*) C. J. Aspley and J. A. G. Williams, *New J. Chem.*, 2001, **25**, 1136–1147; (*c*) K. J. Arm and J. A. G. Williams, *Dalton Trans.*, 2006, 2172–2174; (*d*) Y.-W. Zhong, N. Vila, J. C. Henderson, S. Flores-Torres and H. D. Abrunna, *Inorg. Chem.*, 2007, **46**, 10470–10472; (*e*) O. Johansson and R. Lomoth, *Inorg. Chem.*, 2008, **47**, 5531–5533; For examples of Suzuki coupling on Ir(III) complexes, see ref. 17*e* and 18*c*, and (*f*) W. Leslie, A. S. Batsanov, J. A. K. Howard and J. A. G. Williams, *Dalton Trans.*, 2004, 623–631; (*g*) V. L. Whittle and J. A. G. Williams, *Inorg. Chem.*, 2008, **47**, 6596–6607; (*h*) V. L. Whittle and J. A. G. Williams, *Dalton Trans.*, 2009, 3929–3940.
19 For examples of Sonogashira coupling on polypyridines, see: (*a*) V. Grosshenny, F. M. Romero and R. Ziessel, *J. Org. Chem.*, 1997, **62**, 1491–1500; (*b*) D. Joester, V. Gramlich and F. Diederich, *Helv. Chim. Acta*, 2004, **87**, 2896–2918; (*c*) E. C. Constable, E. Figgemeier, C. E. Housecroft, E. A. Medlycott, M. Neuburger, S. Schaffner and S. Reymann, *Polyhedron*, 2008, **27**, 3601–3606; (*d*) I. Eryazici and G. R. Newkome, *New J. Chem.*, 2009, **33**, 345–357; (*e*) F. Schlütter, A. Wild, A. Winter, M. D. Hager, A. Baumgaertel, C. Friebe and U. S. Schubert, *Macromolecules*, 2010, **43**, 2759–2771; (*f*) J. F. Ayme, J. E. Beves, D. A. Leigh, R. T. McBurney, K. Rissanen and D. Schultz, *Nat. Chem.*, 2012, **4**, 15–20.
20 Previous Sonogashira couplings on polypyridines were performed with a copper(I) co-catalyst, although it has been previously noted that when $Pd(PPh_3)_4$ is used as the catalyst that the presence of copper(I) does not improve yields, see ref. 19*a*.
21 J. Wang and G. S. Hanan, *Synlett*, 2005, 1251–1254.
22 M. A. Bartucci, P. M. Wierzbicki, C. Gwengo, S. Shajan, S. H. Hussain and J. W. Ciszek, *Tetrahedron Lett.*, 2010, **51**, 6839–6842.
23 C. Coudret, *Synth. Commun.*, 1996, **26**, 3543–3547.
24 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204–209.
25 Previous attempts to use Suzuki coupling between pyridine-4-boronic acid and 4′-(4-bromophenyl)tpy have been reported to give poor yields (in DME, 36% yield) ascribed to the electron-withdrawing effect of the pyridine, see ref. 18*b*. We chose to use the 4-pyridineboronic acid pinacol ester due to its easy and large scale preparation despite the lower activity of the ester compared with the free boronic acid.
26 E. C. Constable, *Tetrahedron*, 1992, **48**, 10013–10059.
27 J. E. Beves, E. C. Constable, C. E. Housecroft, M. Neuburger, S. Schaffner and J. A. Zampese, *Inorg. Chem. Commun.*, 2008, **11**, 1006–1008.
28 This complex has been previously reported and characterised by X-ray crystallography, but a synthetic procedure and characterisation was not reported: D. Chartrand, I. Theobald and G. S. Hanan, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m1561.
29 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759–834.
30 Copper-free conditions also gave the products in similar yields, but with longer reaction times, *e.g.* 24 h, 80% for $[Ru(\mathbf{2})_2](PF_6)_2$.
31 (*a*) J. McMurtrie and I. Dance, *CrystEngComm*, 2005, **7**, 216–229; (*b*) J. McMurtrie and I. Dance, *CrystEngComm*, 2010, **12**, 3207–3217.
32 (*a*) E. C. Constable, C. E. Housecroft, M. Neuburger, D. Phillips, P. R. Raithby, E. Schofield, E. Sparr, D. A. Tocher, M. Zehnder and Y. Zimmermann, *J. Chem. Soc., Dalton Trans.*, 2000, 2219–2228; (*b*) E. C. Constable, E. L. Dunphy, C. E. Housecroft, W. Kylberg, M. Neuburger,

S. Schaffner, E. R. Schofield and C. B. Smith, *Chem.–Eur. J.*, 2006, **12**, 4600–4610.
33 J. E. Beves, E. L. Dunphy, E. C. Constable, C. E. Housecroft, C. J. Kepert, M. Neuburger, D. J. Price and S. Schaffner, *Dalton Trans.*, 2008, 386–396.
34 M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.*, 2012, **45**, 1294–1308.
35 To the best of our knowledge. spectroscopic data for $[Fe(tpyph_2)_2](PF_6)_2$ has not been previously reported, so it is given in the ESI.† The X-ray crystal structure has been reported: J. McMurtrie and I. Dance, *CrystEngComm*, 2009, **11**, 1141–1149.
36 M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. C. Thompson, *Inorg. Chem.*, 1995, **34**, 2759–2767.
37 E. C. Constable and A. M. W. C. Thompson, *J. Chem. Soc., Dalton Trans.*, 1994, 1409–1418.
38 M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, 1978, **100**, 5075–5080.
39 P. Thordarson, R. G. E. Coumans, J. A. A. W. Elemans, P. J. Thomassen, J. Visser, A. E. Rowan and R. J. M. Nolte, *Angew. Chem., Int. Ed.*, 2004, **43**, 4755–4759.
40 P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305–1323.
41 For example, the association constant for pyridine by Zntpp in $CDCl_3$ is 900 M^{-1}, see: O. Middel, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 2001, **66**, 3998–4005.
42 (*a*) M. Hoffmann, C. J. Wilson, B. Odell and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2007, **46**, 3122–3125; (*b*) D. V. Kondratuk, L. M. A. Perdigao, M. C. O'Sullivan, S. Svatek, G. Smith, J. N. O'Shea, P. H. Beton and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2012, **51**, 6696–6699.